Appendix A

Method P

AMBIENT AIR ANALYSIS METHOD FOR DETERMINING AMBIENT ATMOSPHERIC CONCENTRATIONS OF SUSPENDED PARTICULATE MATTER NOMINALLY 10 MICROMETERS OR LESS IN AERODYNAMIC DIAMETER (PM10)

1. Principle and Applicability

1.1 Principle

A sampler draws a known quantity of ambient air through an inlet, which is designed to admit specified proportions of particles as a function of their aerodynamic diameter. The inlet is designed to mimic the deposition of particulate matter in the human lung.

The particle collection characteristics of an ideal sampler, one which matches the human lung particle deposition characteristics, are outlined in 5.1.j. The particulate matter collected with such a sampler is referred to as a suspended particulate matter nominally 10 micrometers or less in aerodynamic diameter, or abbreviated as PM10.

As does the human lung, the ideal sampler collects a declining fraction of particles as their diameter increases and an increasing fraction of particles as their diameter decreases. For example, as can be seen in 5.1.j., all particles less than 1.0 Fm in diameter are collected and no particles of 16 or more Fm in diameter are collected.

In the ideal sampler, the PM10 passes through the inlet and is collected on a filter. The net weight (mass) of particulate matter deposited on the filter is determined as the difference in filter weight before and after sampling. The concentration of PM10 is reported as mass of particulate collected per cubic meter of air sampled (micrograms per cubic meter) at normal sea level temperature and pressure (760 torr., 25EC).

1.2 Applicability

This method provides for the measurement in ambient air of the concentration of PM10 over a 24-hour period. The measurement process is nondestructive and the sample can be subjected to subsequent physical and chemical analyses.

2. Range

The lower limit of the mass concentration range is limited by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. The upper range limit is determined by the point at which the sampler can no longer maintain the required flow. This limit is a complex function of particle type and size distribution which is not readily quantifiable.

3. Interferences

3.1 Loss of Volatile Particles

Volatile particles collected on filter material can be lost during shipment and/or storage of the filters. Filters should therefore be reweighed as soon as possible.

3.2 Artifact Particulate Matter

Filters that meet the alkalinity specifications (Section 6, paragraph 6.4) show little or no artifact sulfate. Loss of true nitrate is dependent on location and temperature, but for most locations, the errors are expected to be small.

4. Precision and Accuracy

4.1 Precision

The reproducibility of PM10 samplers must be within $\pm$15 percent of true value at the 95 percent confidence level, as assessed by collocation of samplers.

4.2 Accuracy

Sample accuracy is dependent on sampling effectiveness, flow measurement, and calibration. Sampling effectiveness is expressed as the ratio of the mass concentration of particles of a given size reaching the sample filter to the mass concentration of particles of the same size approaching the sampler. The particle size for 50 percent effectiveness is required to be 10 $\pm$ 1 micrometers.

5. Apparatus and Specifications

5.1 PM10 Sampler

The sampler shall be designed to:

a. draw the air sample, via reduced internal pressure, into the sampler inlet and through the filter at a uniform face velocity.

b. hold and seal the filter in a horizontal position so that sample air is drawn downward through the filter.

c. allow the filter to be installed and removed conveniently.

d. protect the filter and sampler from precipitation and prevent insects and other debris from being sampled.

e. minimize leaks that would cause error in the measurement of the air volume passing through the filter.

f. discharge exhaust air at a sufficient distance from the sampler inlet to minimize the sampling of exhaust air.

g. minimize the collection of dust from the supporting surface.

h. provide uniform distribution of particulate matter on the filter media such that the deposition on the four quadrants shall agree within 5 percent.

The sampler shall operate at a controlled flow rate specified by its designer or manufacturer, and it shall have an inlet system that provides particle size discrimination characteristics meeting all of the specifications in this document. The sampler inlet shall show no significant wind direction dependence. This requirement can generally be satisfied by an inlet shape that is circularly symmetrical about a vertical axis.

The sampler shall provide a means to measure the total flow rate during the sampling period. A continuous flow recorder is recommended. The sampler may be equipped with additional flow measurement devices if it is designed to collect more than one particle size fraction.

The sampler shall have an automatic flow control device capable of adjusting and maintaining the sample flow rate within ±10 percent for the sampler inlet over normal variations in line voltage and filter pressure drop. A convenient means must be provided to temporarily disable the automatic flow control device to allow calibration of the sampler's flow measurement device.

A timing/control device capable of starting and stopping the sampler shall be used to obtain an elapsed run time of 24 ±1 hour (1440 ± 60 minutes). An elapsed time meter, accurate to within 15 minutes, shall be used to measure sampling time. This meter is optional for samplers with continuous flow recorders if the sampling time measurement obtained by means of the recorder meets the ±15-minute accuracy specifications.

The sampler shall have an associated operation or instruction manual.

Since proper service and maintenance is critical to obtaining valid data, the user should adopt adequate and documented standard operating procedures.

5.2 The PM10 sampler shall meet the following criteria for sampling effectiveness at windspeeds from 2 to 24 kilometers per hour:

<u>Parameter</u>	<u>Criteria</u>
Liquid Particles	Expected mass concentration is Within ±10 percent of that predicted By the ideal sampler.
Solid Particles	Expected mass concentration no more than 5 percent above that obtained for liquid particles of the same size.
50 Percent Cutpoint	10 ± 1 Fm aerodynamic diameter
Reproducibility	15 percent coefficient of variation for three collocated samplers.

The sampling effectiveness of the ideal sampler is:

Particle Size (Fm)	Sampling Effectiveness
< 1.0	1.000
2.0	0.942
3.0	0.922
4.0	0.893
5.0	0.857
6.0	0.812
7.0	0.759
8.0	0.697
9.0	0.628
10.0	0.551
11.0	0.465
12.0	0.371
13.0	0.269
14.0	0.159
15.0	0.041
≥ 16.0	0.000

6. Filters

6.1 Filter Medium

No commercially available filter medium is ideal in all respects for all samplers. The user’s goals in sampling determine the relative importance of various filter evaluation criteria (e.g., cost, ease of handling, physical and chemical characteristics, etc.) and consequently determine the choice among acceptable filters. Furthermore, certain types of filters may not be suitable for use with some samplers, particularly under heavy loading conditions (high mass concentrations), because of high or rapid increase in the filter flow resistance that would exceed the capability of the sampler’s automatic flow controller. The specifications given below are minimum requirements to insure acceptability of the filter medium for measurement of PM10 mass concentrations.

6.2 Collection Efficiency

Greater than 99 percent as measured by DOP test (ASTM-2986) with 0.3 Fm particles at the sampler’s operating face velocity.

6.3 Integrity

±5 Fg/m^3 (assuming sampler’s nominal 24-hour air sample volume), measured as the concentration equivalent corresponding to the difference between the initial and final weights of the filter when weighed and handled under simulated sampling conditions (equilibration, initial weighing, placement on inoperative sampler, removal from sampler, re-equilibration, and final weighing).

6.4 Alkalinity

<0.005 milliequivalents/gram of filter as measured by ASTM-D202, following at least two months storage at ambient temperature and relative humidity.

7. Procedure

7.1 The sampler shall be operated in accordance with the general instructions given here and with the specific instructions provided in the sampler manufacturer's instruction manual.

Note: This procedure assumes that the sampler's flow rate calibration was performed using flow rates at ambient conditions (Q_a).

7.2 Inspect each filter for pinholes, particles, and other imperfections; establish a filter information record and assign an identification number to each filter. Careful handling of filters between preweighing and post-sampling is necessary to avoid errors due to damaged filters or loss of particulate.

7.3 Equilibrate each filter in the conditioning environment for at least 24 hours.

Filter Conditioning Environment

a. Temperature range: 15 to 30EC

b. Temperature control: ±3EC

c. Humidity: less than 50 percent relative humidity

7.4 Following equilibration, weigh each filter and record the presampling weight with the filter identification number.

7.5 Analytical Balance

The analytical balance must be suitable for weighing the type and size of filters required by the sampler. The range and sensitivity required will depend on the filter tare weight and mass loading. Typically, an analytical balance with a sensitivity of 0.1 mg is required for high volume SSI samplers (flow rates > 0.5 m^3/min).

7.6 Pre-Run Procedure

a. Air Sample Report – Prior to each run, record on the Air Sample Report: the reporting agency, station address, station name, instrument number and county, site, agency, and project codes. Figure P-1 shows an example of the Air Sample Report form.

b. Clean Filter Installation – the clean particulate filter is placed on the sampler and secured in place.

c. Flow Setting – The actual flow rate must be maintained as specified by the manufacturer in order to maintain the 10 Fm cutpoint of the inlet. This will require special care at elevations greater than 1000 feet above sea level in order to prevent errors due to reduced atmospheric density.

d. Elapsed Time Meter – Record the initial elapsed time meter reading on the Monthly Check Sheet.

7.7 Post-Run Procedure

a. Final Flow Meter Reading – Before removing the filter and flow chart, make sure that the recorder trace shows the final flow. If not, the sampler must be started to determine the final flow.

Remove the flow chart from the recorder and examine the trace for abnormalities. Note and investigate any abrupt changes in air flow. If the start and finish air flows are not representative of your geographic area, note this on the Air Sample Report under “Remarks”.

b. Exposed Filter Removal – Grasp the exposed filter without toughing the darkened area. Fold it in half width-wise with the darkened side in. A satisfactory filter is one which has a uniform white border. Dark streaks into the border may indicate an air leak, which invalidates the sample. If there are insects on the filter, remove them carefully. Note on the Air Sample Report if the filter is torn or ruptured, if the start or finish times are not known, or if the flows are outside the specified range.

Note: A removable filter cartridge may be loaded and unloaded at the station operator’s headquarters to avoid contamination and damage to the filter media.

c. Timer and Elapsed Time Meter Check – After each run, check how long the sampler ran by reading the elapsed time meter. Record the final elapsed time meter (ETM) reading. These ETM readings are used in calculating the concentration of collected particulates as they are more accurate than the time or flow chart times. Adjust the timers to meet the timer acceptance limits of 24 hours ± 15 minutes.

7.8 Equilibration

Equilibrate the exposed filter(s) in the conditioning environment for 24 hours and immediately after equilibration reweigh the filter(s) and record the weight(s) with the filter identification number(s).

8. Calibration

The Size Selective Inlet High Volume Sampler (SSI) is calibrated by establishing that the air sample velocity is designed to meet the particle deposition specifications given in Section 5 of this method. The SSI PM10 sampler is calibrated using an orifice transfer standard that has been standardized against a primary standard Roots meter. The orifice transfer standard is referenced to 25EC and 760 mm Hg. Two different types of orifice calibrators are available. One type uses multihole adapter plates to vary the flow. The second type has an adjustable flow restrictor. In either case, the calibrator is connected to a differential pressure gauge or slack tube manometer. Pressure drops and indicated flow meter readings are recorded and corrected for elevation, as necessary. Using the pressure drops, the standard (true) flowrates are calculated using the certification equation for the transfer standard. Finally, a working sampler calibration curve of standard flowrate vs. indicated flowrate is plotted. The field calibration procedure assumes that:

- elevations below 1,000 feet are equivalent to standard conditions.

- the effect of temperature on the indicated flowrate is negligible and therefore, is not used in the determination of the standard flowrate.

8.1 Apparatus

a. Orifice Calibrator Transfer Standard with certification equation

(1) A flow rate transfer standard, suitable for the flow rate of the sampler and calibrated against a primary standard that is traceable to NBS, must be used to calibrate the sampler’s flow measurement device.

(2) The reproducibility and resolution of the transfer standard must be 2 percent or less of the sampler’s operating flow rate.

(3) The flow rate transfer standard must include a means to vary the sampler flow rate during calibration of the sampler’s flow measurement device.

b. 0-20” differential pressure gauge or slack tube manometer

c. Tygon tubing for static pressure connections

d. Faceplate adapter with “C” clamps

e. Flow charts for continuous recorder

f. Calibration report forms

g. Plastic cap for constant volume sampler sensor

8.2 “As Is” Calibration

Other than routine daily checks, sampler repairs or adjustments (brush changes, motor replacement, flow recorder changes, etc.) should not be made prior to the “as is” calibration. The sampler should be calibrated after each 800 hours of operations, if the sampler is moved to a different site or if the initial flow meter reading falls outside of specified tolerance limits.

Note: Some samplers use a closed loop control system to provide constant blower speed and sampler flow. The flow sensor is located in the throat of the filter holder assembly. Before calibrating this type of sampler, first cover the flow sensor with a plastic cap. After calibrating, remove the cap.

a. Open the PM10 sampler shelter and remove the filter holder. Secure the faceplate adaptor and orifice calibrator; then, tighten down the orifice calibrator. If using a variable resistance calibrator, simply secure the calibrator to the faceplate adaptor and turn the restrictor control fully counterclockwise so that the maximum flow will be obtained. Connect a section of tygon tubing from the orifice tap on the calibrator to one leg of the manometer. Open the other leg so that it is open to the atmosphere. A schematic diagram of a typical sampler flow calibration is shown in Figure P-2.

b. After the sampler has warmed up, turn the motor off and then on and allow the static pressure (ÎP) and indicated flow reading (Qing) to stabilize. Then, read the static pressure (ÎP) and indicated flow readings (Qind). The static pressure is read as the total displacement, in inches, of the manometer water column. Record the static pressure and the indicated flow readings on the PM10 Sampler Calibration Data Sheet (see Figure P-4 as an example). Repeat this step twice so that a total of three test runs are performed.

c. Repeat Step b for each of the remaining four load plates. When using the variable resistance calibrator, select four additional points equally spaced around the setpoint determined in Section 7.6 (two points above and two points below; see example in Figure P-4).

d. Remove the orifice calibrator from the sampler. Measure the indicated flow with a clean filter installed in the PM10 sampler and record this value on the bottom of the Calibration Data Sheet.

e. On the left side of the Calibration Data Sheet, sum the ÎP readings for each line (Runs 1-3) and record the sum under "SUM ÎP"; then calculate and record the average ÎP for each line (Points 1-5). On the right side of the data sheet, sum the Qind readings for each line (Runs 1-3) and record the sum under "SUM Qind"; then, calculate and record the average Qind for each line (Points 1-5).

f. Record the elevation of the sampler on the Calibration Data Sheet. If the elevation is less than 1,000 feet, no altitude correction is required. If the elevation is 1,000 feet or greater, apply an altitude correction factor.

g. Referring to the certification equation and using the corrected ÎP values calculated in f., above (or average ÎP values for locations less than 1,000 feet elevation), determine and record Qstd (transfer standard) for each point, where:

Qstd = Factor Corr ÎP

h. Using the data from the Calibration Data Sheet, plot a Calibration Graph Qstd (transfer standard) vs. Qind. Draw a straight line through the plotted points, or, if facilities are available, obtain a linear regression computer plot.

This line represents the working sampler calibration graph for the particular sampler elevation. A sample plot is shown in Figure P-5.

i. Using the tabulated values of average Qind, determine Qprev (PM10 Sampler) by referring to the <u>previous</u> sampler calibration curve (Qstd vs. Qind). Find the appropriate value of Qprev from the y-axis corresponding to Qind on the X-axis. Record Qprev on the Calibration Data Sheet for each line (points 1-5).

j. Sum the column Qstd (transfer standard), tabulated on the left side of the Calibration Data Sheet. Record this sum as “S_1”.

k. Sum the Column Qprev (PM10 Sampler), determined in Step I; record this sum as “S_2”.

l. Calculate the percent deviation from previous calibration using the equation listed on the bottom of the Calibration Data Sheet. Record the result.

m. Using the sampler calibration graph, convert the clean filter indicated air flow rate to standard air flow rate and record the result on the bottom of the Calibration Data Sheet.

n. Complete a Calibration Report (see Figure P-3). A copy should be kept at the sampling site and in the operating organization’s headquarters file.

8.3 “Final” Calibration – A final calibration is required after specified maintenance is performed (brush changes, motor replacement, flow recorder changes), including maintenance to correct the average initial flow meter reading being out of tolerance, or to repeat a sampler calibration graph which is non-linear.

8.4 Blank Forms and Assistance – a sample copy of forms such as blank Calibration Data Sheets, as well as assistance in calibration procedures, can be obtained by contacting:

STATE OF CALIFORNIA
Air Resources Board
Aerometric Data Division
Quality Assurance Section
P.O. Box 2815
Sacramento, CA 95812

9. Calculations

9.1 Determine the average flow rate over the sampling period corrected to reference conditions as Q_{std}.

9.2 Calculate the total volume of air sampled as:

$v = Q_{std} \times t$

where:

v = total air sampled in standard volume units, std m^3;

t = sampling time, min.

9.3 Calculate the PM10 concentration as:

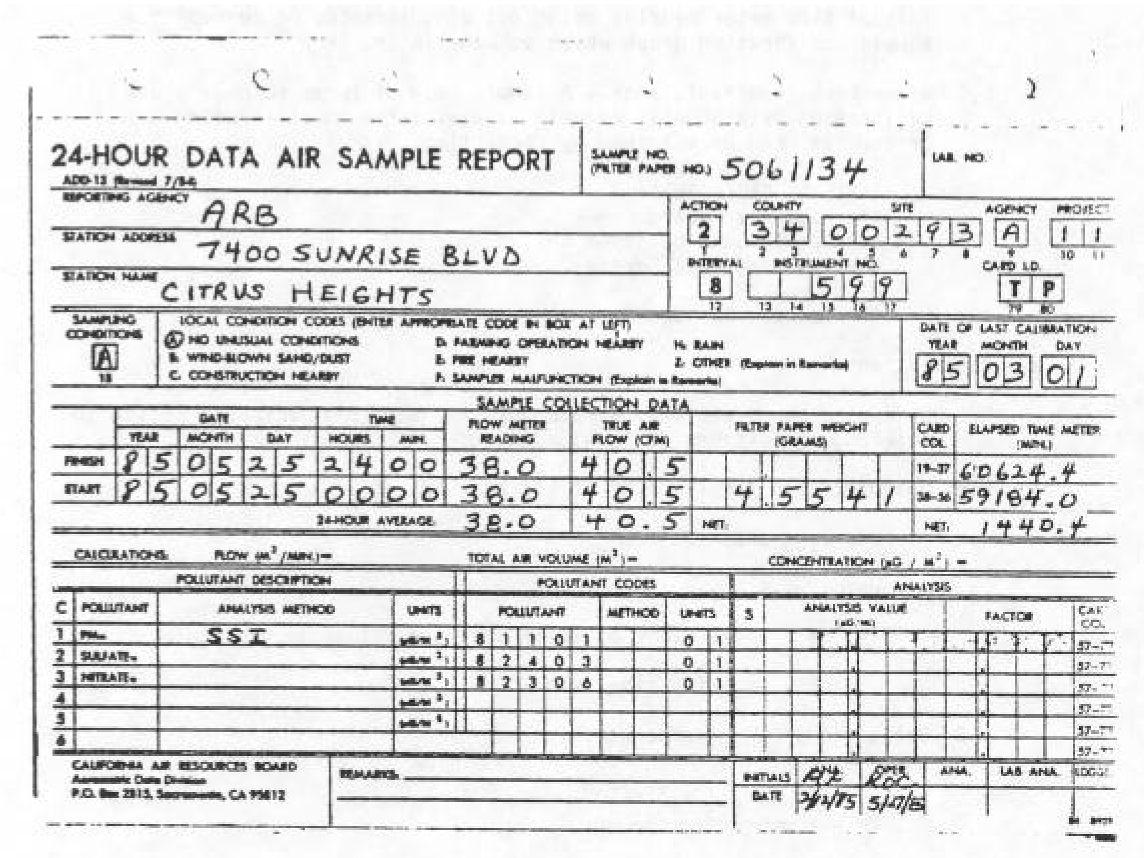
$$PM10 = \frac{(w_f - w_I) \times 10^6}{V}$$

Where:

PM10 = mass concentration of PM10, ug/std m^3;

W_f W_I = final and initial weights of filter(s) Collecting PM10 particles, g;

10^6 = conversion of g to ug.



24-HOUR DATA AIR SAMPLE REPORT

ADD-12 (Revised 7/84)

SAMPLE NO. (FILTER PAPER NO.) 5061134

LAB. NO.

REPORTING AGENCY: ARB

STATION ADDRESS: 7400 SUNRISE BLVD

STATION NAME: CITRUS HEIGHTS

ACTION	COUNTY	SITE	AGENCY	PROJECT
2	34	00293	A	11

INTERVAL	INSTRUMENT NO.	CARD I.D.
8	599	TP

SAMPLING CONDITIONS: A

LOCAL CONDITION CODES (ENTER APPROPRIATE CODE IN BOX AT LEFT)

A. NO UNUSUAL CONDITIONS
B. WIND-BLOWN SAND/DUST
C. CONSTRUCTION NEARBY
D. FARMING OPERATION NEARBY
E. FIRE NEARBY
F. SAMPLER MALFUNCTION (Explain in Remarks)
H. RAIN
Z. OTHER (Explain in Remarks)

DATE OF LAST CALIBRATION: YEAR 85 MONTH 03 DAY 01

SAMPLE COLLECTION DATA

	DATE YEAR	MONTH	DAY	TIME HOURS	MIN.	FLOW METER READING	TRUE AIR FLOW (CFM)	FILTER PAPER WEIGHT (GRAMS)	CARD COL.	ELAPSED TIME METER (MIN.)
FINISH	85	05	25	24	00	38.0	40.5		19-27	60624.4
START	85	05	25	00	00	38.0	40.5	4.5541	28-36	59184.0
24-HOUR AVERAGE						38.0	40.5	NET:	NET:	1440.4

CALCULATIONS: FLOW (M^3/MIN.) = TOTAL AIR VOLUME (M^3) = CONCENTRATION (μG / M^3) =

C	POLLUTANT	ANALYSIS METHOD	UNITS	POLLUTANT CODE	METHOD	UNITS	S	ANALYSIS VALUE	FACTOR	CARD COL.
1	PM10	SSI	µg/m³	81101		01				57-77
2	SULFATE		µg/m³	82403		01				57-77
3	NITRATE		µg/m³	82306		01				57-77
4			µg/m³							57-77
5			µg/m³							57-77
6										57-77

CALIFORNIA AIR RESOURCES BOARD
Aerometric Data Division
P.O. Box 2815, Sacramento, CA 95812

REMARKS:

	ANA.	OPER.	ANA.	LAB ANA.	LOGG.
INITIALS	[illegible]	[illegible]			
DATE	3/4/85	5/27/85			

Figure P-1
24-Hour Data Air Sample Report

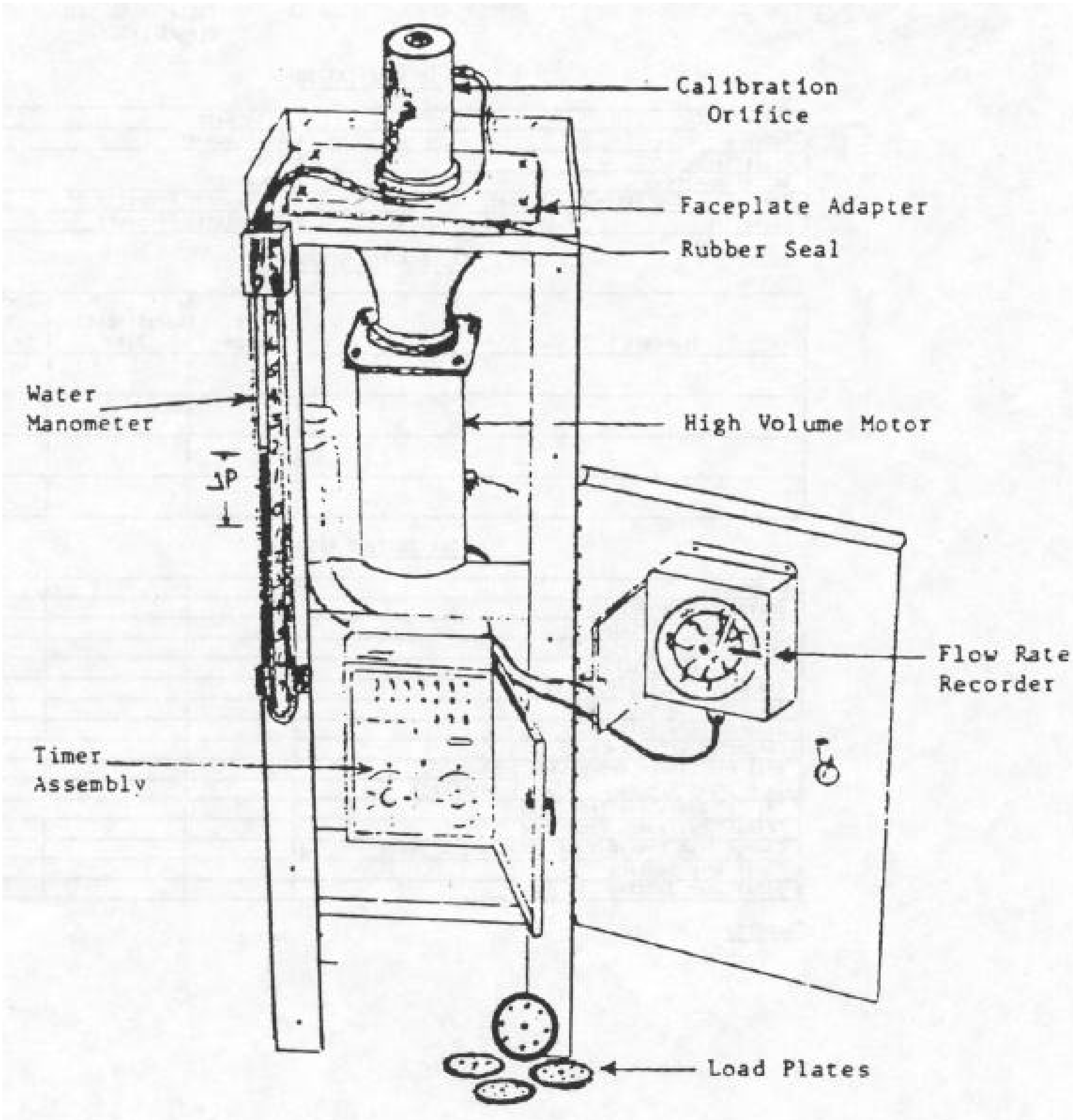


Figure P-2
PM10 Sampler Flow Calibration

CALIFORNIA AIR RESOURCES BOARD
CALIBRATION REPORT

TO:

FROM:

LOG NUMBER:
CALIBRATION DATE:
REPORT DATE:

IDENTIFICATION

Instrument		Site Name
Model Number		Site Number
Property Number		Site
Serial Number		Location
Previous Calibration Log Number		Instrument Property of
Elevation	Site Temperature °C	Barometric Pressure " Hg

CALIBRATION STANDARDS

Standard	I.D. Number	Certification Date	Certified Value Or Factor

CALIBRATION RESULTS

Component					
Instrument Range, ppm					
Initial Zero Setting					
Initial Span Setting					
Air Flow Rate, SLPH					
Air Flow Setting					
Reagent Flow Rate, SCCM					
Reagent Flow Setting					
Converter Efficiency					
Best Fit Linear Regression	Slope				
(x = True; Y =	Intercept				
"As Is" Deviation from True					
"Final" Deviation from True					
Change from Previous Calibration, % (date)					
Final Zero Setting					
Final Span Setting					

Comments

Calibrated By ____________________ Checked By ____________________

ADD-25 (11/84)

Figure P-3
Calibration Report

CALIFORNIA AIR RESOURCES BOARD
HIGH VOLUME SAMPLER/SSI CALIBRATION DATA SHEET

DATE 2/20/85 CALIBRATION: AS IS [ ] Final [X]

LOG NUMBER M 597 INSTRUMENT: HI-VOL [ ] SSI [X] FOR SSI ONLY: HEAD CUT POINT 40 µ

ORIFICE CALIBRATOR TRANSFER STANDARD

Make and Model: BGI
Property Number: 0513
Altitude Correction Factor*: 1.00 (≤1)
Certification Equation: Airflow = 22.5 (factor) $\sqrt{\text{Corr } \Delta P}$

HIGH VOLUME SAMPLER BEING CALIBRATED

Make and Model: GMW
Property No.: 5482 Altitude of Operation: 250'
Property Of: ARB Date Last Calibrated: 8/22/85
Location: Citrus Heights Station No.: 34-293

STATIC PRESSURE ΔP " H_2O			SUM ΔP	AVG ΔP	CORR[1] ΔP	Q_{std} [2]		INDICATED FLOW Q_{ind}			SUM Q_{ind}	AVG Q_{ind}	Q_{prev} [3]
RUN 1	RUN 2	RUN 3	" H_2O	" H_2O	" H_2O	SCFM		RUN 1	RUN 2	RUN 3	—	—	SCFM
4.9	5.0	5.0	14.9	5.0	5.0	50.3	POINT 1	50.0	50.0	49.5	149.5	49.8	49.9
4.0	3.9	4.0	11.9	4.0	4.0	45.0	POINT 2	43.5	44.0	44.5	132.0	44.0	44.7
3.2	3.0	3.0	9.2	3.1	3.1	39.6	POINT 3	38.0	38.0	38.0	114.0	38.0	39.3
2.4	2.4	2.4	7.2	2.4	2.4	34.9	POINT 4	33.0	33.0	32.5	98.5	32.8	34.6
1.8	1.8	1.8	5.4	1.8	1.8	30.2	POINT 5	27.0	28.0	28.0	83.0	27.7	30.0

Summation of Q_{std} (transfer standard), S_1 = 200.0 Summation of Q_{prev} (sampler), S_2 = 198.5

1. Corrected ΔP = Average ΔP x Altitude Correction Factor.
2. Q_{std} (transfer standard) is obtained from the certification equation listed above.
3. Q_{prev} (high volume sampler) is obtained from the last sampler calibration curve (Q_{std} vs. Q_{ind}).

% Deviation from Previous Calibration = $\frac{S_1 - S_2}{S_2} \times 100 = \frac{200 - 198.5}{198.5} \times 100\% = \boxed{+0.8\ \%}$

* Alt. Cor. Fac. = 1.001 x exp (-.0000371 x Altitude, feet) if Altitude >1000 feet; Otherwise = 1.000 (Note: Alt. Cor. Fac. ≤ 1.).

HI-Vol: Clean Filter: Indicated Flowrate = ______; Standard Flowrate = ______ SCFM (Set to 45 SLPM).
SSI: Clean Filter: Indicated Flowrate = 38.5; Standard Flowrate = 40.1 SCFM = 40.1 Actual CFM (Set to 40 Actual CFM).
For SSI Only: Actual CFM = SCFM Altitude Correction Factor.

Comments: ______

ADD-38 (5/85) Calibrated by J. Matson Checked by R. Cleary

Figure P-4
PM10 Sampler Calibration Data Sheet

CALIFORNIA AIR RESOURCES BOARD

High Volume Sampler/SSI Calibration Graph

Log No.: M 597

Station Name: Citrus Heights

Date of Calibration: 2/20/85

Station Site No.: 34-293

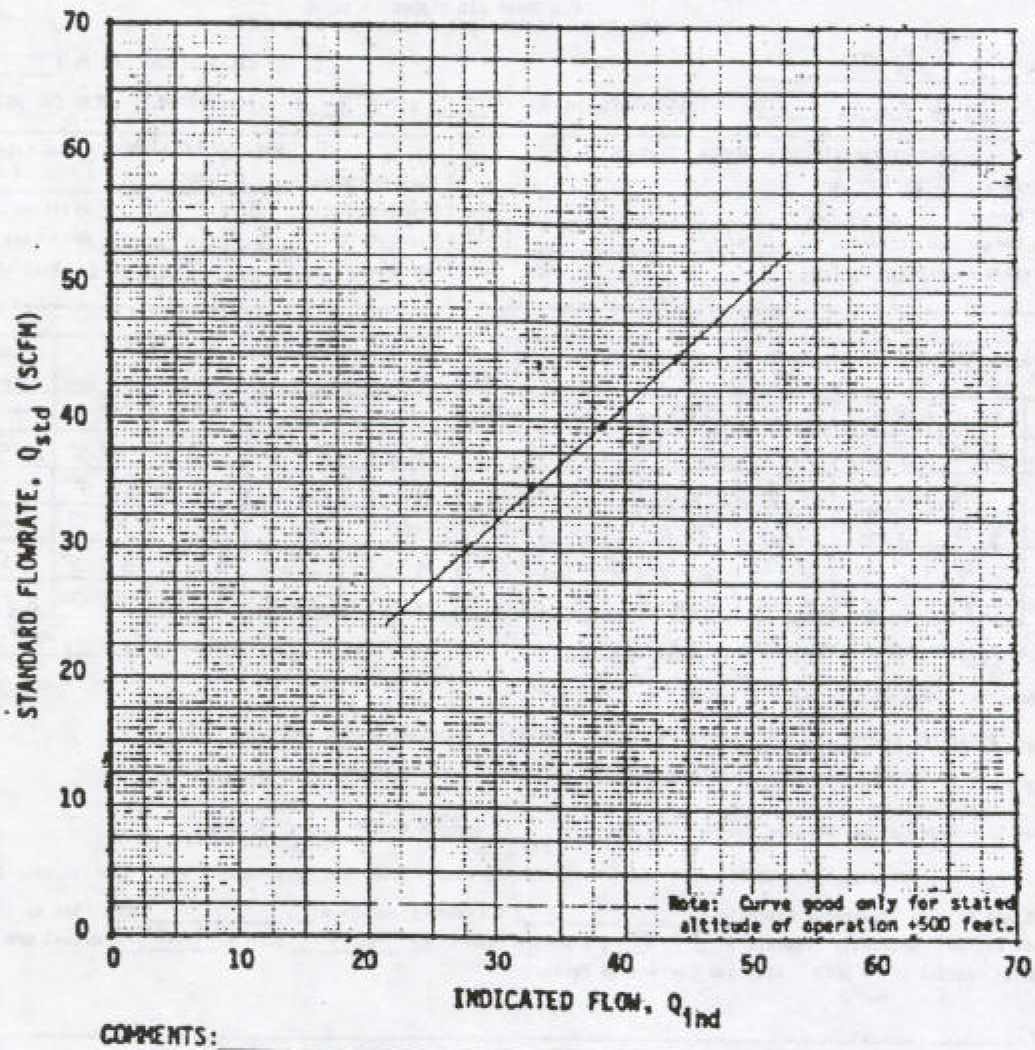
"As Is" Calibration: ______

Sampler Property No.: 0577

Final Calibration: ✓

Sampler Make and Model No.: GMW

Elevation: 250'



COMMENTS: ______

ADD-43 (5/85)

Graph prepared by J. Matson

Figure P-5
PM10 Sampler Calibration Graph